

(12) **UK Patent Application** (19) **GB** (11) **2 386 121** (13) **A**

(43) Date of A Publication 10.09.2003

(21) Application No 0205499.7

(22) Date of Filing 08.03.2002

(71) Applicant(s)

**Alan J Bennetts**  
Crynsal, Main Road, WESTHAY, Somerset,  
BA6 9TN, United Kingdom

**Christopher G Wilde**  
37 St Peter Street, TIVERTON, Devon,  
EX16 6NW, United Kingdom

**Alan Donald Wilson**  
Bargate House, 49 Shepherds Way,  
LIPHOOK, Hampshire, GU30 7HH,  
United Kingdom

(72) Inventor(s)

**Alan J Bennetts**  
**Christopher G Wilde**  
**Alan Donald Wilson**

(51) INT CL<sup>7</sup>

**C09J 4/06 // A61K 6/083**

(52) UK CL (Edition V )

**C3N N6**  
**C3V VAM VBD VEJ VET VEX**  
**C3W W227**  
**U1S S1028 S1034 S1037 S1038 S1367 S1382 S1839**  
**S1854**

(56) Documents Cited

**GB 2374601 A** **GB 1122439 A**  
**WPI Abstract Accession No 1991-114510 &**  
**JP030056580A**  
**WPI Abstract Accession No 1994-002356 &**  
**JP050311126A**

(58) Field of Search

Other: **ONLINE: WPI, JAPIO, EPODOC, CAPLUS**

(74) Agent and/or Address for Service

**Alan J Bennetts**  
**Crynsal, Main Road, WESTHAY, Somerset,**  
**BA6 9TN, United Kingdom**

(54) Abstract Title

**Adhesive cement**

(57) An adhesive cement is prepared by coating an aluminosilicate glass ionomer with an acid polymerization inhibitor of pKa between 2-3.5, and then mixing the treated glass with cyanoacrylate monomer and water. The glass is treated by dissolving the acid, typically tartaric, tartronic, malic, maleic or mellitic acid in methanol and adding the glass powder to form a slurry, then evaporating the methanol. In a further embodiment, the water can also contain a polyacid compound such as polyacrylic acid, polyvinyl phosphonic acid, a copolymer of acrylic acid with itaconic acid and/or vinylphosphonic acid, or mellitic, phytic or tannic acid. In use the cyanoacrylate polymerizes to form a binding resin, whilst the ionomer undergoes an acid-base reaction to form a compound which forms a strong adhesive bond with materials such as metals, glasses, vinyl polymers, or dental material.

GB 2 386 121

**Description of the invention.****HUBS High Strength Universal Bonding and Filling System – Version C6**

The glass-ionomer cement is widely used in dentistry.<sup>1</sup> It consists of two-components: a powder, which is an acid-decomposable aluminosilicate glass and an aqueous solution of a polyacid. The polyacid may be a polymer with acid groups for example a poly (alkenoic acid), a poly (phosphonic acid), a poly(alkenoic/phosphonic acid) or multifunctional oligmers such as mellitic acid, phytic acid or a polyphenol. Sometimes the polyacid in dry form is blended with the glass powder rather than dissolved in water. When these components are mixed together a paste is formed which sets within a few minutes to form a translucent cement, which is suitable for dental applications.

Glass-ionomer cement has the advantage over other dental materials of permanently adhering to tooth enamel and dentine. Comparable dental materials used for restoration of teeth, the composite resin, based on methacrylate polymers, and dental amalgams, can only be attached to tooth material by mechanical or micromechanical means. The nature of the bond between glass-ionomer cement and tooth material – the ionomer *bond* – has not been fully elucidated, but apparently involves the penetration of polyanion chains into the apatite surface, the carboxylate or phosphonate groups of the polymers displacing phosphate groups of apatite. A chemical adhesive bond is thus achieved.

However the glass-ionomer cement has a number of disadvantages. They are weaker than methacrylate polymers and harden and strengthen slowly compared with methacrylate polymers and in the early stages of hardening are susceptible to desiccation.

In order to overcome some of these disadvantages a new class of hybrid material has been developed, the *resin-modified glass-ionomer cement*.<sup>2</sup> these are prepared by mixing an aluminosilicate glass (*ionomer glass*) powder with an aqueous solution of a water-soluble polymer, typically hydroxyethyl methacrylate (HEMA). Suitable polymerization initiators are incorporated in the system. They are dual cure materials that set both by vinyl polymerization and the ionomer cement reaction. These hybrids develop and strengthen more rapidly than glass-ionomer cement. However, although the glass-ionomer cement component has the ability to adhere to tooth material, methacrylates do not have this property, so it is desirable to etch the tooth surface to achieve bonding. HEMA can cause allergic reactions to patients<sup>3</sup>.

Alternatives to methacrylate polymers are the cyanoacrylate polymers. Cyanoacrylate esters are widely used as adhesives as they polymerize when they come into contact with certain solid surfaces.<sup>4</sup> They also have the potential to form filled composites, if mixed with powdered solids. Since cyanoacrylates have adhesive properties these composites would be superior to those based on vinyl polymerization, which lack this property. Thus they would have an advantage over vinyl composites in medical and dental applications.

The principle of the present invention is to incorporate a cyanoacrylate monomer into a glass-ionomer cement formulation. The aluminosilicate glass powder of this cement has basic characteristics and will initiate the polymerization of cyanoacrylate monomers. Polymerization tends to be over vigorous leading to the formation of non-cementitious masses. It is known that cyanoacrylate polymerization of cyanoacrylate s may be inhibited by acids.<sup>5</sup> In this invention polymerization is inhibited by coating the particles with acids (pKa between 2.0 and 3.5). and subsequently initiating polymerization by removing these inhibiting species. Thus, when these powders come into contact with aqueous solutions, an acid-base reaction takes place and the acid is neutralized with increase in nucleophilic character and polymerization takes place.

These cyanoacrylate resin/glass-ionomer cement hybrids represent a new alternative to the methacrylate polymer/glass-ionomer cement hybrids cited above. They are superior to the parent glass-ionomer cement in that that set more rapidly and adhere more rapidly to

surfaces. Moreover, the strength of the adhesive bond is very much greater than glass-ionomer cements because the cyanoacrylate resin bond supplements the ionomer bond. In addition, this hybrid is resistant to desiccation; important in dentistry because desiccating conditions can be encountered in some dental operations. This property also means that extra dental applications can be envisaged. They are also more resistant to acid conditions that sometimes occur in the mouth.

The cyanoacrylate resin/glass-ionomer cement hybrids are also superior to conventional resin-modified glass-ionomer cement based on methacrylate polymers, because the cyanoacrylate polymers are adhesive, whereas methacrylate polymers are not.

These systems consist of a glass-ionomer cement glass/polyacid powder blend that is mixed with a liquid cyanoacrylate monomer to form a hard mass. There are two setting reactions: (i) cyanoacrylate polymerization (ii) the acid-base ionomer reaction which takes place in the presence of water. The presence of glass-ionomer component, which reacts with water, serves to protect the cyanoacrylate moiety against hydrolysis.

The ionomer glass powders may be replaced by other powders of suitable basicity, for example apatite and wollastonite.

## COMPOSITIONS

The materials used in these compositions are a mineral or glass powder of suitable acidobasicity, a liquid cyanoacrylate monomer, an acid retarder and a multifunctional acid. The multifunctional acid may be an acidic polyelectrolyte for example homo- and copolymers of alkenoic acids and phosphonic acids. Alternatively oligomers such as mellitic and phytic acid may be used. The multifunctional acid may be present either in solution or as a dry powder.

### Materials

#### Powder Component

The most suitable powders for these compositions, having the appropriate acidobasicity, are the aluminosilicate glass-ionomer cement glasses. These glasses are prepared by fusing mixtures of silica, alumina, aluminium phosphate, calcium fluoride and cryolite or equivalent materials. The mixture is fused to form a glass at 1100-1300° C and the melt shock cooled by plunging into water. The glass is ground to a fine powder (less than 50µm). The silica content can vary from 27-42%, total alumina 25-39%, phosphate 0-11% (as P<sub>2</sub>O<sub>5</sub>), total fluoride from 0-23%, sodium fluoride from 0-12%. Calcium may be replaced by lanthanum or strontium to impart radio-opacity. These glasses have the property of being decomposed by acids releasing ions into acid solutions

Table 1: Composition of glasses %

	A	B	C	D	E	F	G
Si	19.60	16.33	16.43	18.11	12.51	14.05	14.37
Al	16.41	16.09	16.15	15.41	16.46	13.50	20.38
Ca	8.07	10.64	10.29	5.50	7.07	17.71	20.43
Na	5.12	2.00	2.00	6.08	6.75	2.00	1.56
Zn				2.33			
P	0.96	3.01	3.06	1.31	4.72	2.10	0.00
F	13.10	17.70	17.40	13.80	21.20	20.30	
H				0.18			
O	37.74	34.31	34.58	36.59	31.29	30.04	43.26
Total	101.00	100.10	99.90	99.30	100.00	99.70	100.00

### ***Powder Treatment***

In order to slow down the cyanoacrylate polymerization reaction powders are coated with retarders such as tartaric acid, tartronic acid, mesaconic acid, malic, maleic acid, mellitic acid and similar acids. A suitable method of coating is to dissolve the retarding acid in methanol and then stir in the glass powder to form slurry. The methanol is then allowed to evaporate.

***Polyacid Component.*** The polyacid may be: (i) a homopolymer of acrylic acid or a copolymer of acrylic acid with itaconic acid, or similar unsaturated acid; (ii) a homopolymer of vinylphosphonic acid or similar unsaturated acid; (iii) copolymer of (i) and (ii); (iv) other lower molecular weight, multifunctional oligomeric acids may substituted, for example mellitic acid, phytic acid and tannic acid

***Resin Component.*** The resin component is a liquid cyanoacrylate monomer. A retarder is incorporated to slow down the polymerization reaction. Suitable retardants are: tartaric acid, tartronic acid, mesaconic acid, malic acid and maleic acid.

## **EXAMPLES AND PROPERTIES**

**Example 1 [M34].** 5 parts of a powder blend of the ionomer glass E (Table 1) with 5% of tartaric acid were mixed into 3.35 parts of n-butyl cyanoacrylate. This paste was mixed into 3.35 parts of 40% polyacrylic acid followed by a further 5 parts of the powder blend. The paste set in 18 minutes at room temperature. A compressive strength of 72 MPa was attained in 24 hours.

**Example 2 [P8].** 5 parts of a ground ionomer glass E (Table 1) coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 3.25 parts of a cyanoacrylate (Loctite Super Glue). This paste was then mixed into 2.85 parts of 40% polyacrylic acid followed by a further 5 parts of the ionomer glass powder. The paste set in 4 minutes at room temperature. A compressive strength of 111 MPa was attained in 24 hours. Loctite Super Glue is manufactured by Loctite (Ireland) Ltd

**Example 3 [P9].** 5 parts of a ground ionomer glass E (Table 1) coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 5.25 parts of a cyanoacrylate (Loctite Super Glue). This paste was then mixed into 1.25 parts of 40% polyacrylic acid followed by a further 5 parts of the ionomer glass powder. The paste set in 4.5 minutes at room temperature. A compressive strength of 85 MPa was attained in 24 hours.

**Example 4 [P10].** 10 parts of a ground ionomer glass E (Table 1) coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 6.00 parts of a cyanoacrylate (Loctite Super Glue). The paste set in 7 minutes at room temperature. A compressive strength of 45 MPa was attained in 24 hours.

**Example 5 [P18].** 5 parts of a ground ionomer glass G (Table 1) coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 3.33 parts of a cyanoacrylate (Loctite Super Glue). This paste was then mixed into 3.33 parts of 40% polyacrylic acid followed by a further 5 parts of the ionomer glass powder. The paste set in 20 minutes at room temperature. A compressive strength of 42 MPa was attained in 24 hours.

**Example 6 [L6].** 5 parts of an ionomer glass treated with a polyacid and tartaric acid (Diamond powder) were mixed into 1.54 parts of a cyanoacrylate monomer (Loctite Super Glue). This paste was mixed in to 1.54 parts of an aqueous solution of a polyacid (Diamond Liquid) followed by a further 5 parts of Diamond powder. The paste set in 6 minutes at room temperature. A compressive strength of 96 MPa was attained in 24 hours. (Diamond is manufactured by Associated Dental Products Ltd, Swindon)

**Example 7 [N5].** 5 parts of Diamond powder were mixed into 2.55 parts of a cyanoacrylate monomer (Loctite Super Glue). This paste was mixed in to 2.55 parts of Diamond liquid followed by a further 5 parts of Diamond powder. The paste set in 10 minutes at room temperature. A compressive strength of 103 MPa was attained in 24 hours. This strength compared with 72 MPa for the parent Diamond glass-ionomer cement.

**Example 8 [M2].** 5 parts of Diamond powder were mixed into 1.90 parts of n-butyl cyanoacrylate. This paste was mixed in to 2.2 parts of Diamond liquid followed by a further 5 parts of Diamond powder. The paste set in 10 minutes at room temperature. A compressive strength of 72 MPa was attained in 24 hours. This strength compared with 72 MPa for the parent Diamond glass-ionomer cement.

**Example 9 [M23].** 5 parts of an ionomer glass treated with a polyacid and tartaric acid (Ketac-cem powder) were mixed into 1.90 parts of n-butyl cyanoacrylate. This paste was mixed in to 2.0 parts of an aqueous solution of a polyacid (Ketac-cem liquid) followed by a further 5 parts of Ketac-cem powder. The paste set in 20 minutes at room temperature. A compressive strength of 96 MPa was attained in 24 hours. This strength compared with 78 MPa for the parent Ketac-cem glass-ionomer cement. (Ketac-cem is manufactured by ESPE GmbH, Seefeld, Germany)

**Example 10 [N10].** 5 parts of Ketac-cem powder were mixed into 1.60 parts of a cyanoacrylate monomer (Loctite Super Glue). This paste was mixed in to 2.0 parts of Ketac-cem Liquid followed by a further 5 parts of Ketac-cem powder. The paste set in 10 minutes at room temperature. A compressive strength of 98 MPa was attained in 24 hours. This strength compared with 78 MPa for the parent Ketac-cem glass-ionomer cement.

**Example 11 [L7].** 6 parts of Diamond powder (a blend of an ionomer glass and a anhydrous polyacid) was mixed with 2 parts of a cyanoacrylate monomer (Loctite Super Glue) (manufactured by Loctite. The paste was activated by mixing in 1 part of water. The cement set in 3 minutes at room temperature and developed a compressive strength of 76 MPa.

**Example 12 [P5].** 10 parts of a hydroxyapatite powder coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 13 parts Loctite Super Glue. The paste set in 12 minutes at room temperature. A compressive strength of 40 MPa was attained in 24 hours.

**Example 13 [P6].** 10 parts of a hydroxyapatite powder coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 10 parts Loctite Super Glue and then 0.85 water. The paste set in 6.5 minutes at room temperature. A compressive strength of 38 MPa was attained in 24 hours.

**Example 14 [P11].** 10 parts of wollastonite powder coated with 5% of tartaric acid and 5% polyacrylic acid were mixed into 6.9 parts Loctite Super Glue. The paste set in 9 minutes at room temperature. A compressive strength of 80 MPa was attained in 24 hours.

#### ***Adhesion and Hydrolytic Stability***

Examples 1-14 above bonded to metals and alloys, oxides and silicates, glasses and ceramics, organic polymers (including polymethacrylates, polycarbonates and polytetrafluoroethylene), dental porcelain, dental enamel and dentine, and bone. The adhesive bond was hydrolytically stable for at least 6 months.

**Example 15 [AB]** Cements (glass-ionomer cement/cyanoacrylate hybrid) were prepared from a blend of Diamond powder and Loctite Super Glue cyanoacrylate. This composition was employed to bond steel bolt heads.

The test method used to evaluate the strength of the bond was to record the torque required to shear the cement. The test samples were all stainless steel 14mm bolts the heads of which were roughened with a file and then cleaned with cellulose thinners. Two bolt heads were cemented together with a 1mm (approx) layer of cement separating the two steel surfaces. The bolts were supported vertically and the cement curing accelerated by spraying the bolts with a fine mist of distilled water. The Araldite and glass-ionomer cement/cyanoacrylate hybrids were allowed to cure at temperatures of 5-20 °C for at least 24 hours. The glass-ionomer cement/cyanoacrylate bonds were set after a few minutes where the araldite took at least 30 minutes to harden.

To establish a bench mark against which the cement could be judged twelve trials were undertaken using the bolts and Araldite Rapide, an epoxy general purpose cement universally obtainable and widely used where high bond strength is a desired feature.

A number of mixes were made of Araldite and the glass-ionomer cement/cyanoacrylate hybrid leading to results that fairly reflect the scatter that a user of Araldite and glass-ionomer cement/Cyanoacrylate might expect of when mixed in normal (non controlled environments).

#### **Shear strength test procedure.**

One half of the bonded bolt pair was secured held in a vice while the other side of the joint was inserted in a torque wrench. This particular method of applying a torque load is rather more severe than pure shear testing due to the unbalanced nature of the load. A torque wrench is a cantilever lever device and as such there is unbalanced translational force acting on the bond. This effect was to all intents and purposes the same for all the trials and so can be discounted but it will have inserted an offset into the data as compared to a true shear test.

The initial Torque setting was put at 20NM and then the wrench was pulled smoothly. If the bond did not break this procedure was repeated at 5NM intervals until the bond broke, sample results and the average from the trials are recorded in Tables 2 and 3.

***Table 2 Bond strengths where cure temperature was 18-20 degrees C***

Cement	Bond Strength NM Test 1	Bond Strength NM Test 2	Bond Strength NM Test 3	Average of tests NM
Araldite	35	45	45	42
GIC/cyanoacrylate	40	48	60	49

**Table3 Bond strengths where cure temperature was 5-8 degrees C**

Cement	Bond Strength NM Test 1	Bond Strength NM Test 2	Bond Strength NM Test 3	Average of Tests NM
Araldite	20	20	20	20
Araldite	20	20	25	21
GIC/cyanoacrylate	58	65		62

### Conclusions

The glass-ionomer cement/cyanoacrylate exhibits a stronger bond than Araldite while being as easy to mix. glass-ionomer cement/cyanoacrylate hybrids on setting were found to be immediately resistant towards aqueous solutions unlike the parent glass-ionomer cement. They were also resistant to desiccation. The bond of glass-ionomer cement/cyanoacrylate hybrids to copper was found to be stable for at least 12 months in water, resistant to desiccation and to cycling between moist and dry conditions.

### APPLICATIONS

This invention has application as a multi-purpose high strength material and adhesive. It has use as a versatile surgical cement and adhesive. It may be used, in pre-fabricated form, for implants and prosthesis. In dentistry compositions will find applications as adhesives, as restorative materials, luting agents, liners and as endodontic cements. Because of their adhesive property they are particularly useful in keyhole techniques and in atraumatic field dentistry. These compositions have applications in the adhesion and insulation of electrical components, particularly in regard to the aerospace industry. They can also be used as plaster and Portland cement substitutes and as materials for repair of car bodies.

### REFERENCES

1. Wilson, A.D. & Nicholson, J.W. (1993) Acid-base cements: Their biomedical and Industrial Applications, Cambridge University Press
2. McLean, J.W., Nicholson, J.W. & Wilson, A.D. (1994) Proposed nomenclature for glass-ionomer dental cements and related materials. 25: 587-589
3. Moore, M.M., Burke, F.J.T. and Felix, D.H. (2000) Allergy to a Common Component of Resin-bonding Systems: A Case Report. Dental Update 27: 432-434
4. Millett, G H (1986) Cyanoacrylate Adhesives in Structural Adhesives: Chemistry and Technology, Editor S R Harston, Chapter 6, New York and London, Plenum Press
5. Atsugi Research Institute (1984) Electrically conductive powder for mixing with cyanoacrylates and electrically curable composition using the same. European Patent Application 84113218.6

# **CLAIMS**

**We claim:**

- (1) A High Strength Universal Bonding and filling System formulated upon rapid setting compositions based on mixing aluminosilicate ionomer glasses coated with acid inhibitors with cyanoacrylate monomers and water. Polymerization of the cyanoacrylate occurs when the aluminosilicate glass powder neutralizes the acid inhibitor.**
- (2) A High Strength Universal Bonding and filling System as in claim 1 where the acid inhibitor is a multifunctional carboxylic or hydroxycarboxylic acid.**
- (3) A High Strength Universal Bonding and filling System as in Claim 1 and 2 where water is replaced by aqueous solutions of polyacids. The polyacid may be: (i) a homopolymer of acrylic acid or a copolymer of acrylic acid with itaconic acid, or similar unsaturated acid; (ii) a homopolymer of vinylphosphonic acid or similar unsaturated acid; (iii) copolymer of (i) and (ii); (iv) other lower molecular weight, multifunctional acids may substituted, for example mellitic acid and phytic acid. These are dual setting systems where the cyanoacrylate polymerization is supplemented by an acid-base ionomer setting reaction. These acids may also be incorporated in the powder**
- (4) A High Strength Universal Bonding and filling System as in Claim 1 and 2 where additionally a dry polyacid is incorporated in the powder.**
- (5) A high strength universal bonding system as in claims 1-4 with excellent adhesion to: (a) metals and alloys, including aluminium, nickel, galvanised steel, mild steel, gold, silver and silver-tin alloys (b) glasses and ceramics, including glass-ionomer glasses and dental porcelain (c) organic polymers, including vinyl polymers polytetrafluoroethylene and (d) natural materials including dental enamel and dentine and bone.**
- (6) A high strength universal bonding system as in claims 5 with excellent resistance to desiccation**
- (7) A high strength universal bonding system as in claim 6 with excellent resistance to being immersed in water and weak acids.**
- (8) A high strength universal bonding system as in claim 7 with excellent resistance to being immersed in oil.**
- (9) A high strength universal bonding and filling system as in claim 8 with excellent resistance to pressure and vacuum.**
- (10) A plaster material made from the composition according to according to any of the claims 4-9.**



- (11) A Portland cement substitute made from the composition according to any of the claims 4-9.
- (12) A high strength-bonding agent as in claims 4-9 as a multi-purpose surgical cement and adhesive. In particular in dentistry they have use as dental adhesives, restorative materials, luting agents, liners and as endodontic cements. Also they have applications where minimal drilling is desirable, as in keyhole techniques, or where drilling is not possible, as in atraumatic field dentistry.
- (13) A pre-fabricated surgical implant or prosthesis made from compositions according to any of the claims 4-9.
- (14) Materials for repair of car bodies and the bonding of metals etc. made from compositions according to according to any of the claims 4-9.
- (15) A material for the adhesion and insulation of electrical components, particularly in regard to the aerospace industry made from compositions according to any of the claims 4-9.
- (16) The use of cyanoacrylate monomers to form the resin component of a new type of resin containing glass-ionomer cement.
- (17) The use of ionomer aluminosilicate glasses as the filler constituent of the hybrid materials
- (18) The inhibiting of the cyanoacrylate polymerization by coating the ionomer glass particles with an inhibiting acid with a pKa of between 2.0 and 3.5.
- (19) The coating of ionomer glass particles with inhibiting acids by dissolving the acid in methanol and depositing the acid on the particles by evaporation.
- (20) Initiation of cyanoacrylate anionic polymerization by removal of the inhibiting acid coating the ionomer glass particles by a combination of solution and neutralization



INVESTOR IN PEOPLE

**Application No:** GB 0205499.7  
**Claims searched:** 1-20

**Examiner:** Jason Scott  
**Date of search:** 15 April 2003

## Patents Act 1977 : Search Report under Section 17

### Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X, E	1-18	GB 2374601 A	BENNETTS et al See claim 21 and example 6 which includes tartaric acid.
X	16 & 17	GB 1122439 A	TAKEUCHI See whole document and in particular claim 1 and example 4.
X	16 & 17	WPI Abstract Accession No 1991-114510 & JP 3056580 A ALPHA KK (12.03.91) See abstract	
X	16	WPI Abstract Accession No 1994-002356 & JP 5311126 A ASAHI GLASS CO LTD (22.11.93) See abstract	

### Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>v</sup>:

--

Worldwide search of patent documents classified in the following areas of the IPC<sup>7</sup>:

--

The following online and other databases have been used in the preparation of this search report:

ONLINE: WPI, JAPIO, EPODOC, CAPLUS
------------------------------------